

Electronic structure and magnetic state of transuranium metals under pressure

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Electronic structure of bcc Np, fcc Pu, Am, and Cm pure metals under pressure has been investigated employing the LDA+ U method with spin-orbit coupling (LDA+ U +SO). Magnetic state of the actinide ions was analyzed in both LS and jj coupling schemes to reveal the applicability of corresponding coupling bases. It was demonstrated that whereas Pu and Am are well described within the jj coupling scheme, Np and Cm can be described appropriately neither in $\{m\sigma\}$, nor in $\{jm_j\}$ basis, due to intermediate coupling scheme realizing in these metals that requires some finer treatment. The LDA+ U +SO results for the considered transuranium metals reveal bands broadening and gradual $5f$ electron delocalization under pressure.

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Prominent structural transition from δ - to α -phase of plutonium gives substantial total volume contraction [1]. In americium and curium the similar transitions were also found under high pressure or increasing temperature [2, 3]. These volume collapses are usually related to the drastic electron delocalization. In curium, additional magnetic stabilization of intermediate phases was also found [3, 4].

In many strongly correlated materials Coulomb and Hund interactions are dominant, whereas spin-orbit (SO) coupling is comparably smaller and usually can be treated within various perturbative techniques. In the case of $5f$ electronic shell of actinide metals all these three terms in Hamiltonian are of comparable strength. That results in a very sensitive (non)magnetic ground state, but also in coupling schemes varying from usual LS (Russel-Saunders) one. An intermediate or jj coupling schemes were found to be more appropriate for $5f$ electrons in transuranium metals [5, 6, 7, 8].

In actinide elements spin-orbit coupling is stronger than exchange Hund interaction, and hence the jj coupling scheme can be valid with a well defined total moment \mathbf{J} , but in this case spin \mathbf{S} and orbital \mathbf{L} moments are not well defined. Then the basis of eigenfunctions of total moment operator $\{jm_j\}$ is the best choice, since the matrix of spin-orbit coupling operator and occupation matrix are diagonal in this basis. However the exchange interaction (spin-polarization) term in the Hamiltonian is not diagonal.

In some $5f$ elements intermediate coupling scheme is realized, then the occupation matrix has nondiagonal elements in both $\{m\sigma\}$ and $\{jm_j\}$ orbital bases. Therefore, both terms in the Hamiltonian: spin-orbit coupling and exchange interaction, should be taken in a general nondiagonal matrix form.

Numerous band methods and approximations have been applied to describe magnetic and spectral properties of transuranium metals, see [5] for review. Nonmagnetic ground state of pure plutonium metal observed experimentally [9] was reproduced in the electronic structure calculations in the LDA+ U +SO calculations [10] (local density approximation supplemented with the Hubbard U -correction and spin-orbit coupling). In these calculations the exchange interaction was found to be the reason of artificial antiferromagnetic ordering in various LSDA+ U investigations. Also non-magnetic ground state was found in around-mean-field version of the LDA+ U method [11], and later on within LDA + Hubbard I approximation [12], and also hybrid density functionals with a dominant contribution of HF functional [13]. Recently, the reliability of these results was supported by more detailed analysis of exchange interaction [14], and also in the LDA+DMFT calculations [15], supplementing LDA with the Dynamical Mean-Field Theory [16] (DMFT) [17, 18, 19, 20].

While consistent interpretation of spectroscopic data is not found yet [21], the LDA+ U +SO method provides realistic magnetic state and allows one to estimate elec-

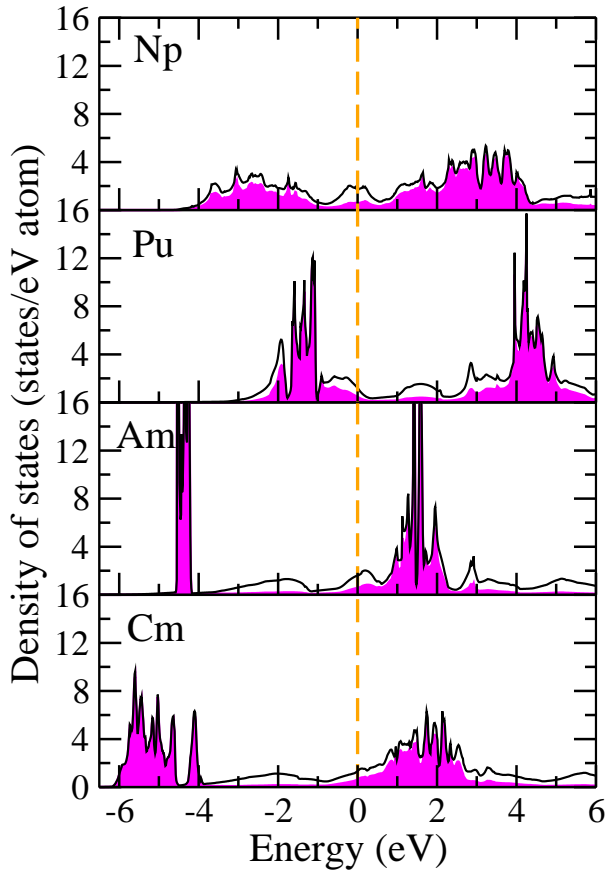


FIG. 1. The density of states: total (solid line) and 5f (shaded area) states of bcc Np, fcc Pu, Am, and Cm from the LDA+ U +SO calculation. The Fermi energy corresponds to zero.

trical resistivity in actinide metals [22] and alloys [23] in good agreement with experimental data.

In this paper electronic structure of bcc Np, fcc Pu, Am, and Cm pure metals was calculated within the LDA+ U +SO method introduced in detail in Ref. [10]. In the method the exchange interaction (spin polarization) term in the Hamiltonian is implemented in a general nondiagonal matrix form regarding the spin variables. This form is necessary for correct description of 5f electrons behavior for the cases of jj and intermediate coupling types.

In the LDA+ U +SO method accounting for strong electron correlations includes Coulomb interaction matrix elements which can be expressed via direct U and exchange J_H Coulomb parameters. A reliable way to estimate these parameters is provided by the constrain LDA approach [24]. To calculate a value of U parameter, in this procedure one evaluates a *screened* Coulomb interaction of 5f electrons which requires the choice of

screening channels taken into account. For s , p , and d channels for bcc Np and fcc Pu, Am, and Cm the constrain LDA calculations resulted in the Coulomb parameter value $U = 4$ eV [10, 17]. The exchange Coulomb parameter J_H is evaluated as the *difference* of interaction energy for the electrons pairs with the opposite and the same spin directions. Parameter J_H does not depend on the screening channels choice. For neptunium and plutonium, the value of Hund exchange parameter J_H was calculated as $J_H = 0.48$ eV [10], for americium as 0.49 eV, and for curium as 0.52 eV [22]. In this work in all LDA+ U +SO calculations we used these exact values of J_H for each actinide metal, since (non)magnetic state of actinide metals is sensitive to the value of J_H [10].

Strong spin-orbit coupling of 5f electrons results in a splitting of the f band into subbands corresponding to the values of total moment $j=5/2$ and $j=7/2$. The value of this splitting is 1 – 1.5 eV. Taking into account Coulomb correlations via the LDA+ U correction does not change qualitatively the band structure, only the separation between subbands increases from 1.5 eV to 5 eV according to the value of $U = 4$ eV.

The density of states (DOS) from the LDA+ U +SO calculations for Np, Pu, Am, and Cm at ambient pressure are shown in Fig. 1. In all DOSs one can distinguish two groups of bands: $j=5/2$ at the lower energies and $j=7/2$ at higher ones. In Np the $j=5/2$ subband is partially filled. From Pu to Cm the Fermi level is shifted upward from the upper slope of $j=5/2$ subband in Pu and crosses the $j=7/2$ subband in Cm due to the increasing number of f electrons. These results are for the metals at ambient pressure in the cubic phases. We used the same lattice parameters as in our previous work [23].

To model the pressure, we assume it to be uniform and applied as a cell volume contraction. While experimentally crystal structure of these metals transforms from cubic to complicated structures like orthorhombic and monoclinic, for the electronic structure and magnetic state of the actinide ion the main result of the applied pressure comes from the contraction of the unit cell volume per ion. In Figs. 2–5 one can find density of states (DOS) for the cubic phases under pressure, real phases with corresponding volumes per ion are referred to in brackets. In the actinide metals under investigation the cubic phases do not correspond to the largest volume per ion, for this reason we also consider some volumes exceeding the cubic volume at ambient pressure.

Neptunium metal. – Magnetic ground state for Np at ambient pressure was found in our calculation (see

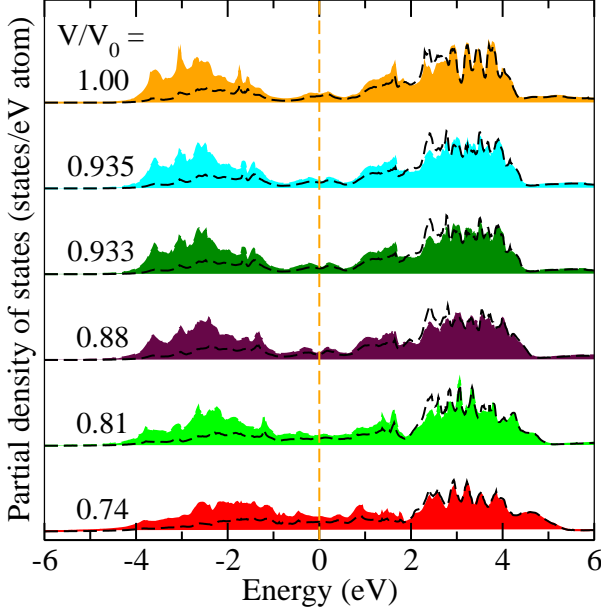


FIG. 2. The partial DOS for the $j=5/2$ (shaded area) and $j=7/2$ (dashed line) subbands of bcc neptunium under pressure obtained from the LDA+ U +SO calculations. For each curve the relative volume V/V_0 is given. The Fermi energy corresponds to zero.

Table 1). Large values of the off-diagonal elements (OD) in Table 1 in both $\{m\sigma\}$ and $\{jm_j\}$ bases evidence for intermediate coupling type in this actinide metal. Four largest eigenvalues close to the unit give f^4 configuration. Upon applied pressure the density of states at the Fermi energy increases, see Fig. 2, effective magnetic moment μ_{eff}^{calc} ranges from $2.55 \mu_B$ to $2.33 \mu_B$.

Plutonium metal. – The LDA+ U +SO calculations for metallic Pu fcc structure (fcc phase in Pu is named δ -phase) at all volumes gave a nonmagnetic ground state with zero values of spin \mathbf{S} , orbital \mathbf{L} , and total \mathbf{J} moments [10] in agreement with numerous experimental data [9]. The occupation matrix has six eigenvalues close to unit, see Table 1 (for details, see Ref. [10]), and is nearly diagonal in the $\{jm_j\}$ basis of eigenfunctions of total moment \mathbf{J} . That gives a f^6 configuration of Pu ion in jj coupling scheme. In Fig. 3 the partial densities of states for $f^{5/2}$ and $f^{7/2}$ subshell of Pu in all volumes (applied pressures) are presented. The DOSes as well as the occupation matrix demonstrate almost completely filled $f^{5/2}$ band with the Fermi level on the top of it and an empty $f^{7/2}$ band. The separation between the centers of these bands is $\approx 5.2 - 5.4$ eV. For small volumes $j=5/2$ subband does not change its position but its bandwidth becomes approx. 1 eV larger.

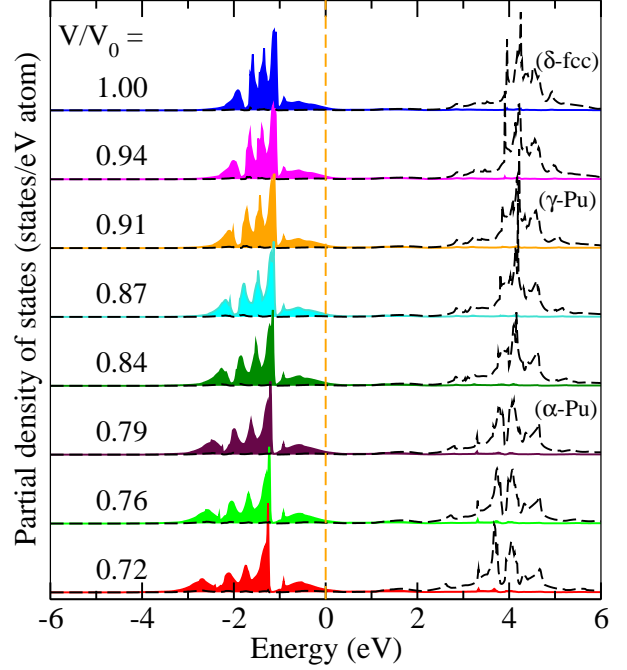


FIG. 3. The partial DOS for the $j = 5/2$ (shaded area) and $j = 7/2$ (dashed line) subbands of fcc plutonium under pressure obtained from the LDA+ U +SO calculations. For each curve the relative volume V/V_0 is given. Real phases with corresponding volumes per ion are cited in brackets. The Fermi energy corresponds to zero.

Americium metal. – The calculated DOSes of Am are shown in Fig. 4. One can see that $j=5/2$ subband is fully occupied that corresponds to f^6 configuration whereas $j=7/2$ subband is almost empty. The occupation matrix has six largest eigenvalues of close to unit, see Table 1. The Fermi level in Am is shifted towards $j=7/2$ subband comparing to Pu due to additional valence electron (see Fig. 4) that occupies s , p , and d states (not shown separately). Note, that the $5f$ bandwidth in Am is smaller than in Pu due to the larger cell volume per ion. Having a delicate balance between SO and exchange interactions, calculated $5f$ -DOS occupied $5f$ band is centered around 4 eV in agreement with Am photoemission spectra that demonstrate large density of states in the range $(-4 \text{ eV}; -2 \text{ eV})$ [25]. The LDA+ U +SO calculations for Am gave a nonmagnetic ground state in all volumes with the $5f$ shell with $S = L = J = 0$ in agreement with experimental data [2].

Curium metal. – In curium $f^{7/2}$ subband is partially filled, providing a peculiar empty state well below the Fermi level, see Fig. 5. The LDA+ U +SO calculation results in S and L moments listed in Table 1. The value of effective magnetic moment μ_{eff}^{calc} calculated from the

TABLE 1. Electronic configuration of $5f$ shell in Np, Pu, Am, and Cm ions in the cubic phases calculated within the LDA+ U +SO method. The largest values of occupation matrices off-diagonal elements OD_{LS} and OD_{jmj} in the corresponding basis sets are given in the second and third columns. Then the seven largest eigenvalues of occupation matrix are presented. The columns from the eleventh to thirteenth show the calculated values for spin (S), orbital (L), total (J) moments.

Metal	OD_{LS}	OD_{jmj}	Largest eigenvalues							S	L	J
Np	0.36	0.46	0.05	0.09	0.26	0.89	0.91	0.91	0.92	1.40	4.68	3.28
Pu	0.45	0.01	0.03	0.92	0.92	0.93	0.93	0.93	0.93	0	0	0
Am	0.47	0.02	0.07	0.97	0.98	0.98	0.98	0.99	0.99	0	0	0
Cm	0.31	0.45	0.10	0.99	1.00	1.00	1.00	1.00	1.00	2.77	0.75	3.52

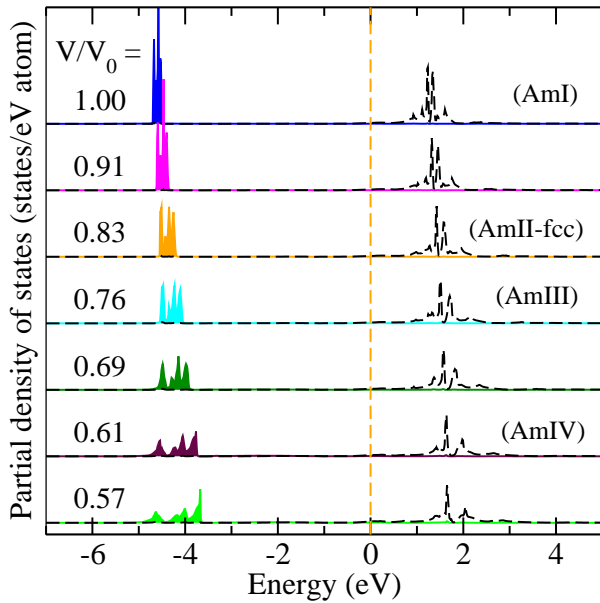


FIG. 4. The partial DOS for the $j = 5/2$ (shaded area) and $j = 7/2$ (dashed line) subbands of fcc americium obtained from the LDA+ U +SO calculations. For each curve the relative volume V/V_0 is given. Real phases with corresponding volumes per ion are cited in brackets. The Fermi energy corresponds to zero.

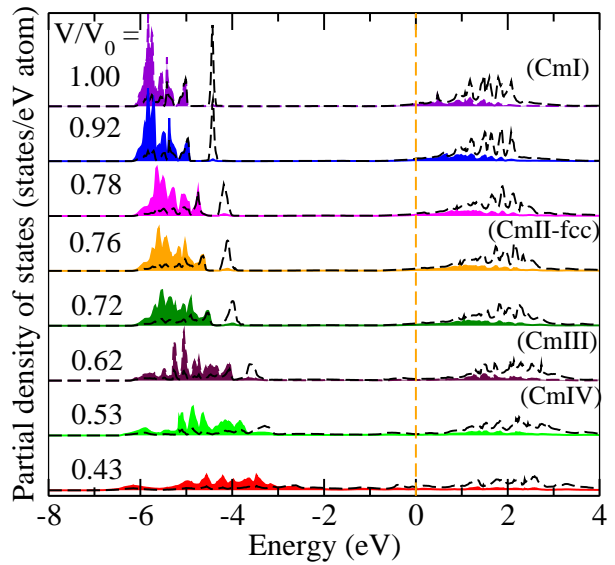


FIG. 5. The partial DOS for the $j = 5/2$ (shaded area) and $j = 7/2$ (dashed line) subbands of fcc curium obtained from the LDA+ U +SO calculations. For each curve the relative volume V/V_0 , where V_0 is the volume at ambient pressure, is given. Real phases with corresponding volumes per ion are cited in brackets. The Fermi energy corresponds to zero.

total moment value J by the method used in Ref. [10] for different volumes gradually decreases from $7.44 \mu_B$ for the largest volume (corresponding to the volume per ion in the CmI phase) to $6.86 \mu_B$ (CmIV). This result corresponds to the model calculations assuming in pure LS coupling the magnetic moment of the curium ion to be $7.94 \mu_B$, but for a realistic model of intermediate coupling lowering up to $7.6 \mu_B$ [26], while experimentally the magnetic moment was reported as $7.85 \mu_B$ [26].

In conclusion, we have calculated the electronic structure of bcc Np, fcc Pu, Am, and Cm pure metals within the LDA+ U +SO method under applied pressure in assumption of uniform unit cell contraction. Static

mean-field approach used in this work results in gradual (featureless) electron delocalization and bands broadening under pressure. While jj coupling scheme is well suited for description of Pu and Am ground state, for Np metal only intermediate coupling scheme seems to be appropriate, whereas in Cm the intermediate coupling is closer to LS -type. We suggest accounting for dynamical correlations effects will allow one to reproduce not only the delocalization of $5f$ electrons under applied pressure but also will resolve some fine feature of this process.

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